

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Decomposition of Sulfide Minerals

We, TEXAS GULF SULPHUR COMPANY, a corporation organised under the laws of the State of Texas, United States of America, of 75 East 45th Street, New York 17, State of New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to the decomposition of sulfide-containing minerals, and particularly to the interaction of sulfide-containing minerals with a chlorinating agent such as free chlorine or available chlorine in chlorine compounds, so as to produce sulfur and metal chlorides, the latter being thereafter treated and recovered as desired by methods known in the art. One of the objects of the invention is to provide an improved process for extracting sulfur from sulfide-containing minerals. A further object of the invention is to decompose such minerals by means of their reaction with chlorine, either elemental or in easily decomposable chlorine compounds, in such a way as to render available for recovery the sulfur and the corresponding metal chlorides in a manner which obviates the disadvantages inherent in prior art processes.

The reactions between metal sulfides and chlorine have long been known, and in fact proposals have been made to utilize these reactions as a means of decomposing the sulfide minerals to produce sulfur and metal chlorides. Since in such processes an essential step is the removal of sulfur formed in the reaction, some prior art processes have involved operations at temperatures above the distillation range of sulfur or under such lower temperature conditions as would nevertheless permit of volatilization of the sulfur substantially as quickly as it is formed. Such processes, however, have not been successful in practice. The reasons for their failure have been manifold, but two important reasons

were the difficulties in providing apparatus capable of withstanding the effects of chlorine and of its by-products under the conditions and also the fact that the ferrous chloride formed interfered with the complete reaction of the ore with the chlorine.

It has been found that by operating at a relatively low temperature, i.e. between 100° and 440° C. we can achieve rapid and economical reaction of the mineral sulfides together with adequate removal of products and by-products from the surface of the sulfide particles, provided that the operation is carried out in the presence of a considerable volume of liquid, as more fully described below.

Among the sulfide-containing minerals which lend themselves to treatment by the novel process of the invention are the sulfides of iron, such as pyrites and pyrrhotite. However, nonferrous metal sulfides can also be treated by the process of the invention, as well as iron sulfides containing non-ferrous metal sulfides and mixtures of iron and non-ferrous metal sulfides.

As a source of chlorine, there may be used any chlorinating agent, such as free chlorine, sulfur chlorides, or ferric chloride.

Operation may be at atmospheric or super-atmospheric pressures, and although sub-atmospheric pressure operation is not precluded, it has not been found to be advantageous.

The general process of the decomposition of iron sulfides with chlorine depends mainly upon the following reactions: $\text{FeS}_2 + \text{Cl}_2 = \text{FeCl}_2 + 2\text{S}$ and $\text{FeS} + \text{Cl}_2 = \text{FeCl}_2 + \text{S}$, from which it will be observed that ferrous chloride and sulfur are formed. These will naturally both be produced on the surface of the sulfide which comes in contact with the chlorine. At temperatures in the range of the invention the sulfur will be present as a liquid and the ferrous chloride as a solid. The density of ferrous chloride is considerably lower than that of the metal sulfides and it will tend

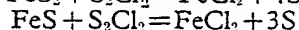
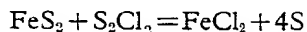
to envelop the sulfide particles and to shield them from further decomposition. At the same time the sulfur produced in the reaction further tends to shield the particles.

5 It has been found that when the reaction is carried out in the presence of liquids having the properties described below the stated disadvantages are overcome. Numerous inorganic and organic liquids are suitable for the purpose of the invention provided that they dissolve the chlorinating agent used, or chlorine liberated therefrom, preferably without reaction. However, a liquid medium that reacts with the chlorinating agent is satisfactory provided that excessive amounts of acids or other unwanted by-products are not formed and that the reaction is either readily reversible or yields a product which itself will chlorinate the metal sulfide.

20 Examples of inorganic substances which are reactive with chlorine and which may be used in the process of the invention are sulfur and the various sulfur chlorides.

25 Since the primary function of the added liquid in the process is to remove from the surface of the metal sulfides the sulfur and metal chlorides formed in the reaction, it is necessary that the liquid be present in considerable amounts relative to the sulfides. We have found that from 2 to 10 times as much liquid by weight as metal sulfide is effective. It is also essential that good agitation be provided so that the washing action of the liquid will be fully utilized.

35 When sulfur is used as such a liquid, some of the chlorine may react with the sulfur to form sulfur chlorides. However, this does not interfere with the overall operation of the process because sulfur chlorides in turn react with iron sulfides according to the reactions:—



45 Moreover, as is well known, the reaction between sulfur and chlorine to form sulfur chlorides is reversible and at the higher temperatures within the range of the invention the equilibrium is in the direction of the elements instead of the compound. However, the precise manner in which the reactions occur is not critical.

50 The annexed drawing shows, in flow-diagram form, one embodiment of the invention, in which sulfur is used as the liquid and elemental chlorine as the primary chlorinating agent.

55 In carrying out the invention by the process illustrated in the drawing, finely ground sulfide mineral, such as iron sulfide, suitably dried by means known in the art, is introduced into a bulk or stream of molten sulfur. As shown in the diagram, the sulfide may be introduced through line 1, the chlorine through line 2, and the sulfur through line 3 into a reaction vessel 4 which is provided with

mixers, propellers, circulating pumps, or other efficient agitating means. As set forth above, from 2 to 10 parts by weight of sulfur are present for each part of sulfide. In Stage 1 the chlorine is preferably present in less than stoichiometric proportions, the reaction being completed in Stage 2. Products leaving reactor 4 through line 5 include a suspension of metal chloride, together with unreacted sulfide, in sulfur. These products pass into a settler or thickener 6 in which a major part of the liquid sulfur is separated from the solid metal chloride. Depending on the ratio of chlorine and sulfides used in Stage 1, the sulfur may contain more or less of the sulfur chlorides formed by the reaction between sulfur and chlorine. However, we prefer to operate with an excess of sulfides in Stage 1, so that any sulfur chlorides present will be completely reacted. The amount of sulfur drawn off settler 6 through line 7 will be approximately the amount produced by the reaction, the bulk of the sulfur in the system being recycled. The bottoms from settler 6, which include metal chlorides, unreacted sulfide and sulfur, are passed through line 8 into a second stage reaction vessel 9. In reactor 9 the sulfides remaining unreacted in Stage 1 are further chlorinated in the presence of an excess of the liquid sulfur so as to completely decompose the sulfide chlorine being fed through line 10. Under these conditions, where sulfur is the liquid, it may not be possible to prevent the formation of some sulfur chlorides which will remain in solution in the sulfur. However, after passing through line 11 into settler 12 the sulfur containing sulfur chloride impurities is recycled, in part to reactor 9 and in part to reactor 4 where it comes in contact with fresh sulfides under such conditions as regards temperature, ratio of reactants and the like as to be freed from sulfur chloride.

Ferrous chloride is removed from settler 12 in solid form along with nonferrous metal chlorides formed from nonferrous metal sulfides admixed with or present in the iron sulfide. The ferrous chloride may be converted to ferric chloride by methods known in the art or may be heated with air or oxygen to convert it into ferric oxide with liberation of chlorine which is then recycled to the reactor of Stage 2 through line 10 with such make-up chlorine as is necessary.

Another alternative, which is preferred is to react the mixture of ferrous chloride and sulfur which is derived from the main process with ferric chloride, thereby releasing sulfur chlorides and producing ferrous chloride. The ferrous chloride, after separation of any excess sulfur, is oxidized by air or oxygen to form the ferric chloride used in the first step together with an amount of iron oxide corresponding to the iron content of the ferrous chloride contained in the ferrous chloride-sulfur mixture. The ferrous chloride-sulfur

mixture used in the reaction with ferric chloride should carry about 35% of sulfur and often will contain as much as 50% of sulfur by weight. The sulfur chlorides produced may be passed directly to the main process, to function as a chlorinating agent, or recovered for further utilization as a chlorinating agent or otherwise as desired. A cyclic flow of iron chloride is provided, in which the iron changes from the ferric to the ferrous condition and back again, while ferrous chloride from the main reaction is essentially converted to ferric oxide.

When liquids other than sulfur are used, the flow will, of course, be modified as necessary to separate the sulfur formed. The nature of the modification will depend upon the characteristics of the liquid.

Following are examples of the process as carried out on a laboratory scale using sulfur as the liquid:—

EXAMPLE 1.

A mixture of 100 pounds of pyrite at minus 200 mesh (U.S. standard) was suspended in 500 pounds of molten sulfur. The temperature of the mass was raised to 349° C. and chlorine gas was passed into the mixture at a rate of 20 pounds per hour. At the end of 2½ hours 98.1% of the metal sulfide content of the pyrite had been decomposed, the temperature having meantime risen to 390° C.

EXAMPLE 2.

One hundred pounds of pyrite, together with 385 pounds of sulfur were treated with sulfur chloride in a reaction vessel fitted with a stirrer. The temperature was raised initially to 340° C. and the addition of sulfur chloride was spread over three hours. Ninety-six per cent of the metallic content of the pyrite was converted.

EXAMPLE 3.

One part of pyrite, 10 parts of sulfur and 1 part of sulfur dichloride were heated in a sealed tube at 360° C. for one hour 95% of the iron content of the pyrites was converted to ferrous chloride.

WHAT WE CLAIM IS:—

1. A process of decomposing metal sulfides to obtain sulfur and a metal chloride which comprises reacting a metal sulfide with a chlorinating agent at a temperature between 100 and 440° C. in the presence of from 2 to 10 parts by weight for each part of said metal sulfide of a liquid which is a solvent for said

chlorinating agent whereby said liquid effects removal of reaction products from the surfaces of the said sulfide and affords access of the chlorinating agent to said surfaces.

2. A process according to Claim 1, in which the chlorinating agent is chlorine.

3. A process according to Claim 1, in which the chlorinating agent is ferric chloride.

4. A process according to Claim 1, in which the chlorinating agent is a chloride of sulfur.

5. A process according to any one of the preceding claims, in which the liquid solvent is liquid sulfur.

6. A process according to any one of the preceding claims, in which the metal sulfide is iron sulfide.

7. A process according to any one of the preceding claims, in which the metal sulfide is suspended in the liquid in finely ground form, the chlorinating agent is passed into the suspension thereby converting the metal sulfide into sulfur and a metal chloride.

8. A process according to Claims 6 and 7 which includes reacting the ferrous chloride and sulfur mixture with ferric chloride to produce further ferrous chloride, and sulfur chlorides, removing sulfur chlorides and separating excess sulfur and oxidizing the ferrous chloride to form ferric chloride which is recycled, and iron oxide, which is recovered.

9. A process according to Claim 7, which comprises commingling the metal sulfide in finely divided form with the liquid, agitating the resulting mixture, continuously adding a chlorinating agent to said mixture in a reaction zone, continuously withdrawing a suspension comprising reaction products from said zone, and separating solids comprising metal chloride from said suspension.

10. A process according to Claim 9, which includes continuously separating sulfur substantially in the amounts formed in the reaction from the suspension.

11. A process according to Claim 10 which includes returning at least part of the liquid separated from the suspension to the reaction zone.

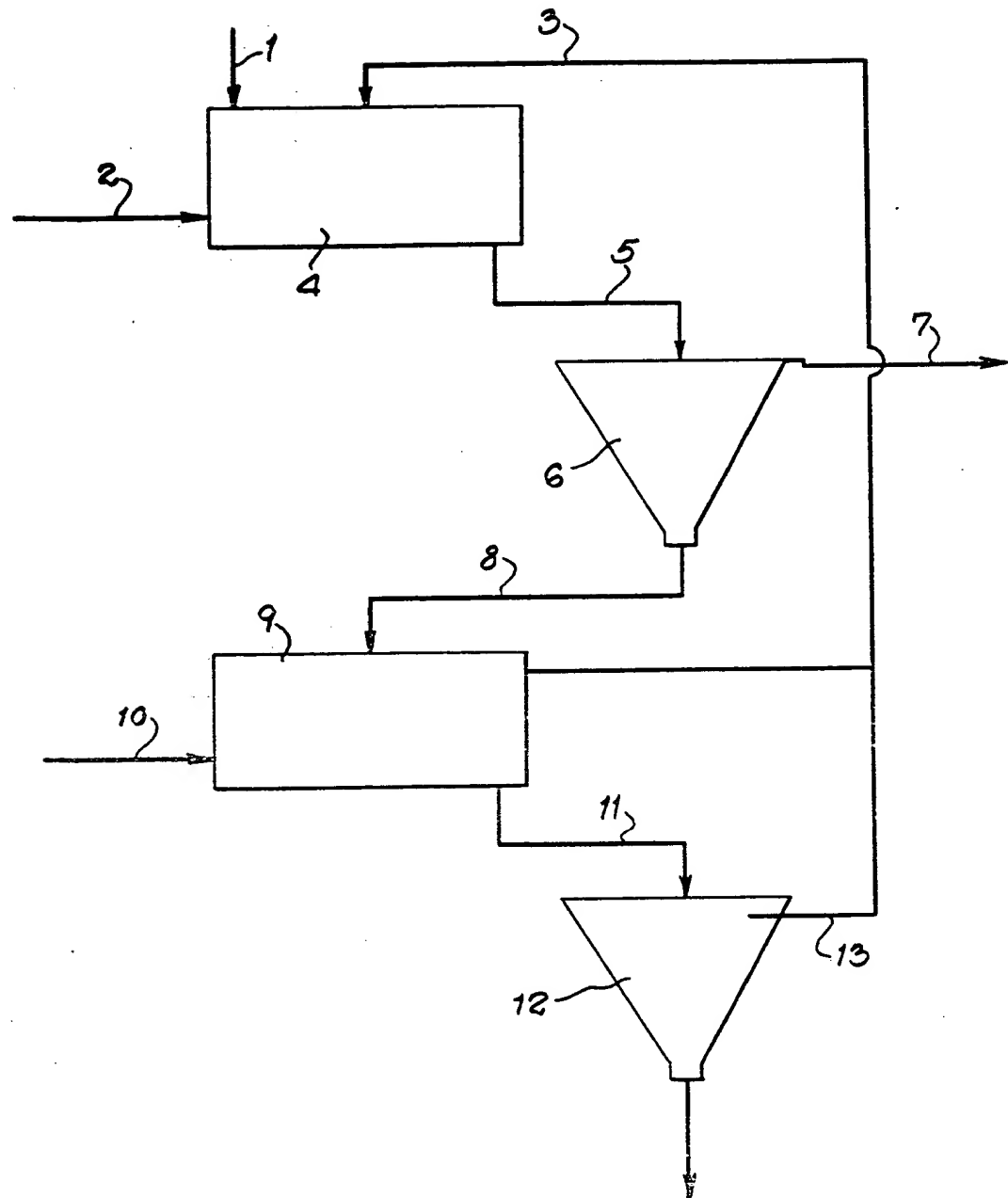
12. A process of decomposing metal sulfides to obtain sulfur and a metal chloride substantially as hereinbefore described and as illustrated in the accompanying drawing.

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Chartered Patent Agents,
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COMPLETE SPECIFICATION
*This drawing is a reproduction of
the Original on a reduced scale*



ERRATA

SPECIFICATION NO. 805,922

Page 3, line 44, after "how" insert ".,."

Page 3, lines 48-49, for "sulphides" read "sulfides".

THE PATENT OFFICE,
19th January, 1960

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